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A Study of Molecular Orientation in One-Way Drawn Poly(Ethylene Terephthalate) Films by Means of Polarized Infra-Red Spectroscopy and Birefringence Measurements

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Summary

Polarized infrared spectroscopy and birefringence measurements have been used to study the changes in molecular orientation which occur on homogeneous hot (T = 80°C) and cold (T = 20°C) drawing of poly(ethylene terephthalate) (PET) sheets. Excellent agreement was obtained between the infrared orientation functions for absorption bands associated with 1507 cm^{-1}, 1580 cm^{-1} and 1615 cm^{-1}, C-C stretching mode of the benzene ring, and average orientation functions obtained from optical birefringence. It was confirmed that the Gauche conformer of the ethylene glycol residue in the amorphous phase could be oriented perpendicularly to the draw direction ($\lambda_p<4$). The development of molecular orientation along the specimen axis in the necked sample confirms the entangled nature of the polymer chains in which the natural draw-ratio corresponds to the response of a network stretched up to its maximum of extensibility.

Introduction

The determination of the orientation function using dichroic ratio measurements requires the use of well known absorption bands. The detailed assignment of the absorption bands in the infrared spectrum of PET has been the subject of much controversy. A survey of the literature and a complete absorption band assignment as a function of confirmational structure was recently published (ŠTOKR et al., 1982). The most widely used absorption band to measure crystalline orientation is the 975 cm^{-1} trans band. This band is assigned to the trans CO stretching of the ester group. The dipole moment vector angle α of this vibration with respect to the crystallographic axis chosen as chain axis was experimentally found to be 32° (CUNNINGHAM et al., 1974).

The problem to measure overall or amorphous orientation is a more complex one. Gauche conformational defects appear in the all trans crystalline ethylene glycol residue and cis and trans conformations of the C=O groups may also occur. Such structures forbid the use of the crystallographic axis as a general chain axis. We will consider separately the ethylene glycol fragment and the benzene ring. As far as orientation of the ethylene glycol residue in the amorphous phase is concerned, the 897 cm^{-1} CH_2 rocking mode, related to gauche conformational structures can be used. For such structures the cristallographic axis does not hold any more and one has to consider a local chain axis, for the glycol residue. An 90° angle exists between the dipole moment vector of the vibration under consideration and the local chain axis. It is thus possible to get an insight on the orientation fg of the gauche glycol fragment in the amorphous phase.

On the other hand, some vibrations of the benzene ring are insensitive to conformation (STOKR et al., 1982) and can be used to measure overall orientation of the benzene ring in crystalline and amorphous phase as well. CUNNINGHAM et al., 1974; used the 795 cm^{-1} and 875 cm^{-1} absorption bands to perform such a measurement. Both these bands appear as badly overlapping systems (HUTCHINSON et al., 1980). More the 875 cm^{-1} band absorbance is very strong. As a matter of fact GRIFFITH (1977) has shown that absorbance values no greater than 0.7 absorbance unit had to be used with FT-IR systems for quantitative measurements. Film thickness used in the present study forbid the use of the 875 cm^{-1} band.

Experimental

The experimental part of this section is described in details elsewhere (JASSE et al., 1979; LATROUS et al., 1981; ENGELAERE et al. 1982).

Drawing procedures

The study was conducted with samples of intrinsic viscosity $|\eta|$ = 0.75 ml/g^{-1} ($\overline{Mn}$ = 24 600) from originally amorphous PET sheets kindly supplied by Rhône Poulenc Industries Laboratories. Dumb-bell samples of gauge dimension 20 mm x 5.2 mm were extended to fixed strain in an Instron tensile testing machine at a crosshead speed of 1 $mm.mn^{-1}$ ($\dot{\varepsilon}_o = 5.10^{-4}s^{-1}$). Two deformation processes have been performed :

i) Hot drawing at various draw ratio $\lambda_p = L/L_o$, from 1.4 to 6.1 where L and L_o are the final and original length, respectively. After deformation, all the samples were quickly cooled under tension to room temperature.

ii) Cold drawing at room temperature. In that case the cold drawing at room temperature is a specific quantity called the natural draw-ratio.

Birefringence measurements

Birefringence was measured at room temperature on a Zeiss polarizing microscope with an Ehringhauss compensator. A large number of measurements was made in order obtain statistically meaning-full results.

Average Crystallinity

Average apparent crystallinity values, β, were calculated from density (gradient column containing aqueous solution of calcium nitrate at 23°C) and Differential Scanning Calorimetry (Perkin Elmer model DSC II) results (LATROUS et al., 1981).

Infrared dichroïsm

The polarized spectra were obtained using a Nicolet 7199 Fourrier transform infrared spectrometer. Single-beam spectra were run and the absorbance spectra were calculated using the computer facility and a stored polarizer spectrum as reference. The polarization of the infra-red beam was obtained by the use of a Perkin-Elmer gold wire grid polarizer. A 2 cm^{-1} resolution and 100 co-added scans were used and infrared dichroïsm was calculated as $R = A_{//} / A_{\perp}$, with $A_{//}$ and $A_{\perp}$ the optical densities at the absorption maximum.

Results and discussion

It was interesting to find some more or less isolated absorption bands allowing the determination of overall orientation. In an uniaxially oriented polymer $A = (A_{//} + 2 A_{\perp})3$ is an absorbance invariant with respect to orientation. In Figure 1, $\bar{A}$/e, where e is the film thickness, is plotted as a function of draw ratio λ_p for different bands. The A/e values for the 1580 cm^{-1} and 1615 cm^{-1} C-C stretching modes of the ring are insensitive to orientation. The 1580 cm^{-1} ring C-C stretching should also be usable. However the absorbance of this band is quite strong and a light increase of A/e as a function of draw ratio is observed. Later on we will use the 795 cm^{-1}, 1580 cm^{-1} and 1615 cm^{-1} bands to determine overall orientation. In order to obtain consistent results for both crystalline and amorphous phases the crystallographic axis will be used as chain axis in both cases. Such a choice is supported by the fact that reliable results are obtained when comparing birefringence and infrared measurements (CUNNINGHAM et al., 1974). In such condition, the dipole moment vectors of the vibrations with respect to chain axis are 31° (1580 cm^{-1}) and 60° (1615 cm^{-1}).

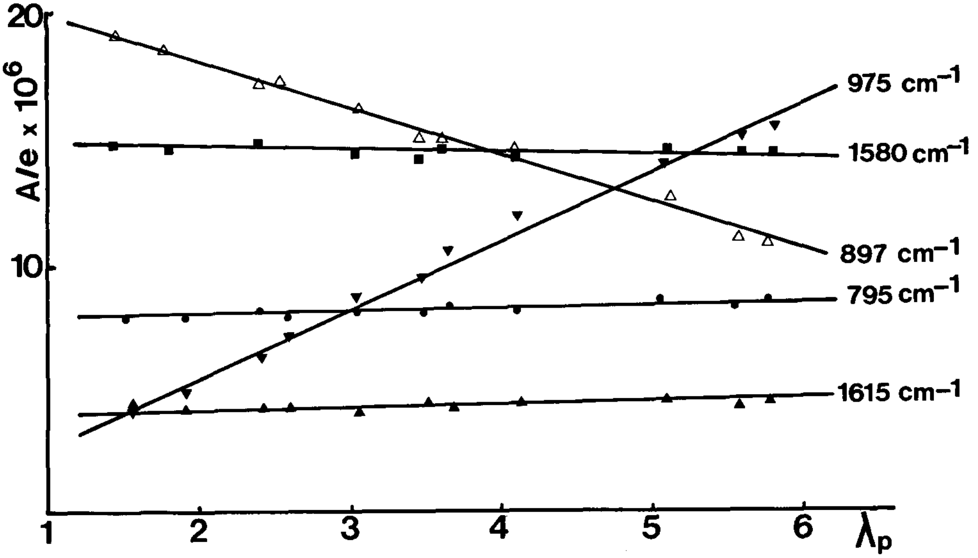

Figure 1. Reduced absorbance, A/e, versus draw ratio, λ_p, of stretched PET film at T = 80°C

Figure 1 shows that a linear relationship holds between A/e versus draw ratio for the 975 cm^{-1} (trans) and 897 cm^{-1} (gauche) absorption bands. The relative amount of trans sequences increases while the gauche amount decreases similarly with increasing draw ratios. No drastic change is observed when orientation induced crystallinity becomes important (λ_p>3). As a matter of fact, the 975 cm^{-1} trans band is related to trans sequences in crystalline phase as well as in amorphous one (KOENIG et al., 1979). Change of trans conformations can only appear in the amorphous phase resulting in an increase of crystallinity when oriented trans amorphous chains concentration is high enough to permit the appearance of crystalline organization.

The complete characterization of partially crystalline films requires a separate estimate of the orientation of crystalline and amorphous regions, as well as their relative proportions, i.e., the crystallinity ratio β. From the usual additivity rule, the additive effect of the optical anisotropy of each phase is represented by the following equation :

$$\Delta n = \beta fc\Delta C^o + (1-\beta) fa\Delta a^o + \Delta nf = \Delta a + \Delta c \qquad (1)$$

where Δnf is the (often assumed negligible) contribution of form birefringence, Δc^o and Δa^o are the intrinsic birefringence per unit volume of a fully oriented polymer in the crystaline and amorphous phase respectively. fc and fa are the orientation functions characterizing the average orientation of the crystalline and amorphous phases respectively.

Intrinsic birefringence Δa^{o} and Δc^{o} were previously measured by different authors (SAMUELS, 1974; De VRIES et al., 1977; DUMBLETON, 1968). A good agreement is observed for $\Delta c^{o} = 0.22$ but discrepancy appears for Δa^{o}. Two recent papers (CAVROT et al., 1982; BIANGARDI, 1980) confirm the value $\Delta a^{o} = 0.27$ previously obtained by DUMBLETON.

The orientation of crystalline phase, fc, often derived from X-ray diffraction and infrared dichroism, can be calculated from Gaylord's theoritical analysis (GAYLORD, 1975) of stress-induced crystallization in Gaussian networks whose results have been shows to be in good agreement with various experimental data (KRIGBAUM et al., 1964; BHATT et al., 1976).

$$fc = \frac{1}{2}\left(\frac{3\lambda_p^3}{2+\lambda_p^3} - 1\right) \qquad (2)$$

The results plotted in Figure 2 show a relatively good agreement between the change of crystalline orientation function versus homogeneous draw ratio, λ_p, according to Gaylord's analysis and the change of second order moment $<P_2(\cos\theta)>$ obtained from the 975 cm^{-1} band by infrared dichroism. It is obvious that for low dra-ratios ($\lambda_p<3$) the measured infrared values are slightly lower than those calculated from Gaylord's function. As this function is relative to crystalline orientation it is plausible to think that this discrepancy is related to the presence of trans sequences less oriented in the amorphous phase than in the crystalline phase. The alignment of the strain-induced molecules into what constitute essentially fibrillar crystalline regions, accounting for some 30 % of the sample at high draw-ratios is also evident from the results obtained from the 975 cm^{-1} band, which is characteristic of extended trans sequences in both crystalline and amorphous regions. There is also a considerable increase in trans orientation in this low-strain region.

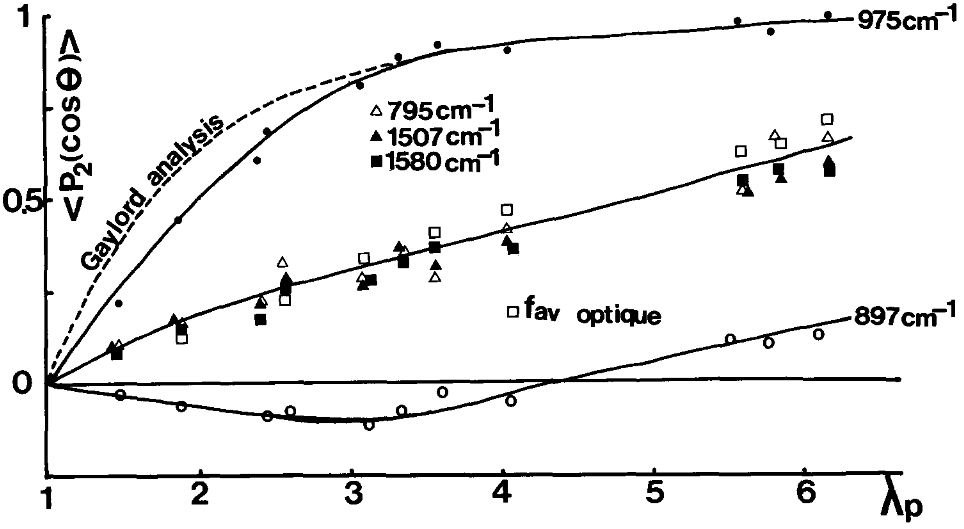

Figure 2. Average orientation function $<P_2(\cos\theta)>av$, against homogeneous draw ratio, λ_p.

The change of the orientation function associated with gauche conformation of the ethylene glycol residue is much more complicated than for the trans one. Figure 2 shows that for draw ratios $\lambda_p<4$, this function becomes slightly negative and pass through a minimum for $\lambda_p = 2.8$ (corresponding to the onset of crystallization). This king of behavior shows that a small strain gauche aliphatic segments can be oriented transversely to the draw direction as previously suggested (CUNNINGHAM et al., 1974). From the infrared experimental fc value and birefringence data, it is possible to calculate the amorphous orientation function fa using relation (1). It is important to keep in mind that the fa function is relative to the amorphous phase as a whole including the aromatic and aliphatic portions ot the chains.

Polymer average orientation function can be expressed as :

$$f_{av} = \beta fc + (1+\beta) fa \qquad (3)$$

In Figure 2 is plotted as a function of draw ratio λ_p the orientation function $<P_2(\cos\theta)>$ obtained from 795 cm^{-1}, 1507 cm^{-1}, 1580 cm^{-1} bands and leading to overall orientation of the benzene ring in crystalline and amorphous phase as well. An attempt was made to correlate the observed dichroïsm with birefringence measurement defined by the average molecular orientation f_{av}. The most striking feature of these plots is their similarity and that both orientation factors are comparable in that they reflect the orientation of the polymer chains in a similar manner through the overall range of draw-ratios.

At low draw-ratios where little or no crystallinity is produced ($\lambda_p<3$) the main cause of the gradual rise in average chain orientation is the presence of entanglements associated with long-chains sequences in a non-crosslinked network structure. Crystallization does not produce here an appreciable sharp increase in molecular orientation but results of a gradual alignment of polymer chains parallel to the direction of stretch. This crystallization serves effectively as a system of semi-permanent crosslinks trapped chain ends up to the limit extensibility of the strain-induced network ($\lambda_p \sim 6.2$).

Cold-drawing

On some semi-crystalline polymers, as PET, the tensile stress-strain curve shows, after yield, a marked fall in the engineering stress which is related to the geometrical thinning of the specimen, and thus, leads to the formation of a neck.

Figure 3 shows that the development of molecular orientation as measured by birefringence and infrared dichroïsm increase with increasing time spent in the neck (i.e. with increasing distance "d" from the shoulder on the centre line along the specimen axis for the neck). These results are very similar to those obtained for PET (RIETSCH et al., 1979) and linear polyethylene (CAPACCIO et al., 1976) in previous investigations. The orientation function $<P_2(\cos\theta)>$ obtained using the 1615 cm^{-1} and 1580 cm^{-1} bands relative to overall orientation of the benzene ring reflects the orientation of the polymer chain in a similar manner as the molecular orientation calculated from birefringence measurements. As shown in Figure 3 when the conditions for stable neck propagation may be attained (d>40 mm) the strain and molecular orientation are essentially uniform throughout the specimen. Thus the crystalline orientation in the completely necked region is close to 1 and the average crystallinity $\beta = 0.29$.

The equation (3) leads to :

$$f_{av} = 0.29\ fc + 0.71\ fa \qquad (4)$$

and

$$\Delta n = 0.191\ fa + 0.064\ fc \qquad (5)$$

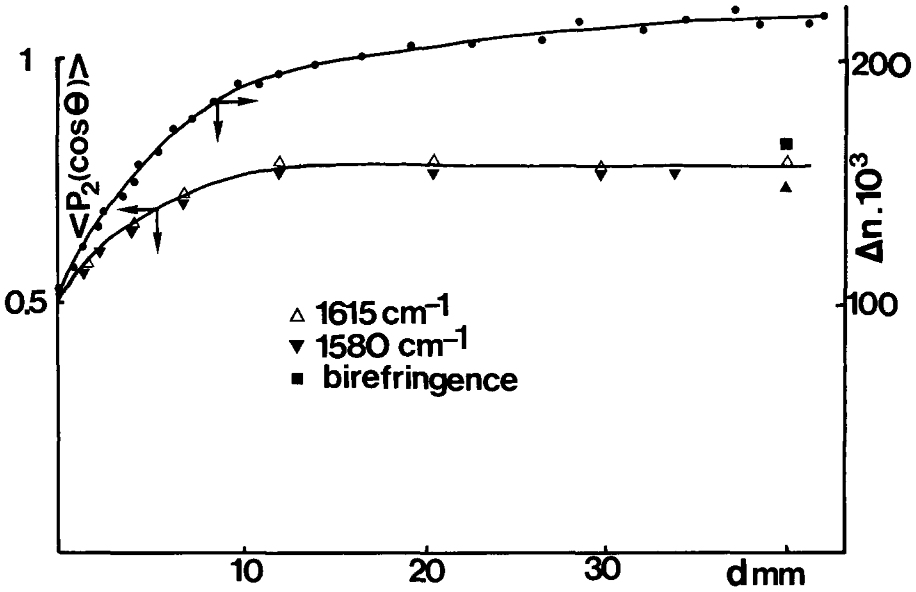

Figure 3. Variation of molecular orientation, at midpoint of neck, versus neck length, d, from the shoulder

combining equations (4) and (5) : $f_a = 0.81$, $f_c = 1$, $f_{av} = 0.86$.

These results are in good agreement with infrared orientation values; f_{av} is slightly superior to the ultimate value obtained in hot-drawn homogeneous deformation ($f_{av} \approx 0.75$) in which necessarily occurs a relative amount of slip between physical entanglements until the limiting draw-ratio.

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